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(54) Abstract Title
Liquid laundry detergent compositions

(57) Liquid laundry detergent compositions provide good detergency for the cleaning of garments and textiles, as well as further providing a germicidal action to textile fabrics in a domestic laundering process and killing dust mites which may be infesting said fabrics. An aqueous, germicidal and acaricidal liquid detergent composition comprises:

A) a major anionic surfactant constituent selected from alkylethercarboxylates and alkylethersulfonates;
B) a cationic germicidal surfactant;
C) a nonionic surfactant preferably selected from alcoholalkoxylates, akylphenol alkoxylates, alkylpolyglycosides, amine oxides and alkanolomides,
D) a compatible optical brightener constituent; and
E) an acaricidal compound effective against dust mites wherein the weight ratio of the cationic surfactant to the major anionic surfactant is 2:1 or greater.

The acaricidal compound may be benzyl benzoate.

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IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOSITIONS

This invention relates to laundry detergent compositions which have germicidal ingredients and are also effective against dust mites.

Background of the Invention

Common house dust is an important cause of asthma, rhinitis, atopic dermatitis, eczema and other allergic conditions in sensitive individuals. Household dust generally comprises a variety of particulate matter including pollen, dust mites, dust mite allergens, dirt, skin cells, animal dander, insect parts, pillow feathers, food particles and mould spores. The particular constituents of dust will depend on location within the house, whether pets are present and other obvious factors. One of the principal sources of allergies is dust mites, which inhabit rugs, carpets, and other fabric surfaces, particularly sofas, mattresses, pillows, upholstered chairs and the like. The mite *Dermatophygoides pteronyssinus* has been identified as a major source of house dust allergen. This mite and the related mites *D. farinae, D. microceras* and *Euroglyphus maynei* are the predominant house dust mites in temperate climates in North America, Europe, Australia and other areas.

Dust mites are not insects, but are eight-legged arachnids, relatives to ticks and spiders. They live in close association with humans (or other mammals), their main food source being the shed scales from skin. Adult mites are approximately 300 microns (3/10 mm) in size, having developed over approximately 25 days through egg, larval and nymph stages. Adults live for 2 to 3-1/2 months, during which time each female can produce about 20-40 eggs. Dust mites are photophobic, living deep in pillows, mattresses, carpets, upholstered furniture and other soft materials.

In addition to a food source, the other essential requirement for dust mite growth is adequate humidity. Dust mites are 75% water by weight. They do not drink water, but must absorb water vapor from the air in order to survive. Specialized glands above their pairs of legs produce secretions high in sodium and potassium chloride, which act to absorb water vapor from surrounding air. This can only be accomplished if the surrounding humidity is sufficiently high. Relative humidities of about 65-80% at temperatures ranging from about 20° to 35°C are optimal for dust mite growth. Dust mites will die at humidities of 50% or less. In geographical areas where humidity is high, dust mites are present in nearly all homes and may be as plentiful as 18,000 mites per gram of dust. Literally millions of mites can inhibit a single bed or rug.

A major dust mite allergen is present in mite faecal particles. Each mite produces about 20 faecal particles per day, and more than 100,000 of them may be present in a gram of dust. These particles vary from about 10 to 40 microns in size, comparable to the size of pollen grains, and become airborne during domestic activity such as making beds and vacuuming carpets.

Group I allergens (dermatophagoides farinae I - Der f I and dermatophagoides pteronyssinus I - Der p I) are heat labile, 24,000 molecular weight glycoproteins (hydrolytic enzymes). These allergens appear to be structural homologues and have very similar N-terminal amino acid sequences. These group I allergens are regarded as the most important and are excreted in their highest concentrations by the mite's gastrointestinal tract in the form of mite's faecal particles, suggesting that they are associated with digestion. They elute rapidly (within 2 minutes) from isolated faecal particles, but very slow from mite bodies.

Group II allergens (Der p II and Der f II) are 15,000 molecular weight proteins with almost identical N-terminal amino acid sequences that are also secreted by the mite's gastrointestinal tract in the form of faecal allergens, although not in as high a concentration as the group I allergens. This suggests

that they probably derived from a source other than the gut. Their actual function has not been determined.

Most mite-allergic individuals produce antibodies to both the group I and group II allergens.

Allergen	Mol. Weight	pH
Group I		
Der p I	24,000	4.6-7.4
Der f I	24,000	4.6-7.4
Group II		
Der p II	15,000	5.0-6.4
Der f II	15,000	7.8-8.3

Acute exposure to mite allergens has been shown to induce wheezing, rhinitis, eustachian tube obstruction or eczema in sensitized patients. Chronic exposure can cause bronchial hyper-reactivity and chronic asthma. There is a correlation between the level of exposure to house dust mite allergen in early childhood and the likelihood of the subsequent development of asthma. Conversely, asthmatics sensitive to dust mites improve in environments without mites, such as at high altitudes or in hospital rooms. Attempts have therefore been made to decrease patients' exposure to dust mites in the home.

Studies of dust avoidance measures in homes have shown that the use of impermeable mattress and pillow encasings and the removal of bedroom carpeting are associated with a decrease in mite counts. These measures have also been shown to be of clinical value, with a decrease in symptoms and medication requirements occurring in children and adults with dust-sensitive asthma when pillows and mattresses are encased and carpets are removed.

Although carpets and upholstered furniture are major sites of dust

mite growth, many allergic individuals are unable or unwilling to remove these from their home. Ordinary vacuuming does not remove dust mites or significantly decrease dust mite allergen levels, and in fact, vacuuming of carpets with the usual household appliances actually increases the amount of airborne dust. However, the use of special filters such as HEPA (High Efficiency Particulate Air) filters or two-ply vacuum bags, and/or the employment of central vacuuming systems (where the dust is collected in a receptacle remote from the room being cleaned) have been helpful. Nevertheless, vacuuming seldom removes all of the live mites, mainly because the mites have little suction cups on the tops of their legs which cause them to cling to textile fibres.

Various chemical agents have been used against mites, including: compounds known under the common names as resuethrin, phenothrin, permethrin, allethrins, tetramethrin, furamethrin, cypermethrin, decamethrin, phenvalerate, phenpropathrin, terallethrin, empenthrin and pyrethrin; pyrethroid compounds such as 1-ethynyl-2-methyl-2-pentenyl-2,2-dimethyl-3,3-(2,2-dichlorovinyl)-cyclopropane-1-carboxylate, 1-ethynyl-2-methyl-2-pentenyl-2,2,3,3-tetramethylcyclopropane-1-carboxylate, ∀-cyano-3-phenoxybenzyl-2,2-dimethyl-3-(2,2,3-tribromethyl)-cyclopropane-1-carboxylate; organic phosphorus compounds such as sumithion, fenthion, tetrachlorvinphos, diazinon and DDVP; and carbamate compounds such as those sold under the trademarks Baygon and Sevin. However, these conventional miticides are expensive and are often either toxic to human beings or have the potential themselves to cause allergic or other adverse reactions. Therefore, the use of such compounds in a household environment cannot be the solution to controlling the population of dust mites.

A number of less toxic miticidal agents have been proposed for use in controlling dust mites. As noted in U.S. Patent No. 4,800,196 to Nomura et al., these include phenyl salicylate, diphenylamine, methyl beta-naphthyl ketone, coumarin, phenethyl benzoate, benzyl salicylate, phenyl benzoate, N-fluorodichloromethylthio-cyclohexene-dicarboxyimide, p-nitrobenzoic acid

methyl ester, p-chlorometaxylenol, "-bromocinnamic aldehyde, 2,5-dichloro-4-bromophenol, N,N-dimethyl-N'-tryl-N'-(fluorodichloromethylthio)-sulphamide, 2-phenylphenol, sodium 2-phenylphenolate, 5-chloro-2-methyl-4-isothiazoline-3-one, 2-methyl-4-isothiazoline-3-one and benzimidazolylmethylcarbamate. These can be used in the form of solutions, wettable powders, granules, sprays, etc.

While many of these compounds have some degree of effectiveness against dust mites, their use is not without attendant shortcomings. For example, many of them are rather expensive to produce and/or may be difficult to form into compositions for ordinary domestic use. Elimination of dust in a household environment is a task which is intensely disliked to the point where the average householder is no longer embarrassed by a moderate layer of dust or the presence of "dust bunnies" under beds or behind furniture. Furthermore, as noted above, dust removal and/or vacuuming often stirs up the dust mites and their attendant allergens and, temporarily at least, causes more distress to allergic persons.

More effective methods of reducing exposure to dust mites and their faecal matter, have been developed which do not depend on the diligence of the householder in removing dust.

U.S. Patent No. 5,271,947 to Miller et al. features the use of finely divided sodium chloride powder as a method for killing mites and controlling their allergen-bearing faeces. The powder has the consistency of talcum powder and is used, for example, by applying the powder with a broom or brush to carpets and other textile materials. However, one of the disadvantages in using sodium chloride powder is its hygroscopicity; if the amount used is not carefully controlled, the salt will absorb moisture from the air, particularly in humid climates.

One of the more effective agents for killing dust mites is benzyl benzoate, a compound which is readily available and inexpensive. Powder formulations containing benzyl benzoate are commercially available for application to carpets. British Patent No. 1,368,657 teaches the use of a

composition for treating bedding and similar materials which comprises benzyl benzoate and polyethylene glycol, or an ether or ester thereof, as an evaporation retarding agent. British Patent No. 2,042,893 teaches the use of a composition comprising benzyl benzoate and a fatty acid ester for application to bedding and also for treating the skin. A similar composition for general miticidal use in households is taught in published Japanese Patent Application No. 61-91103.

More generally, U.S. Patent No. 4,666,940 to Bischoff teaches the use of various miticidal agents, including particularly benzyl benzoate, as a component in cleansing compositions. The disclosed compositions can also contain dissolved or dispersed plastic materials, but said materials must form discrete particles of particular size and must not form a film.

In an article by G. Schober et al., "Control of House-Dust Mites (Pyroglyphidae) with Home Disinfectants", Experimental & Applied Acarology 3:179-89 (1987), the authors provide data showing that the addition of benzyl benzoate to certain commercially available carpet cleaning formulations results in a composition with better acaricidal properties than other known acaricides.

U.S. Patent No. 5,180,586 to Sato et al. discloses that certain compounds, previously known for use as perfuming agents in foods and cosmetics, have been found to be effective in killing dust mites.

To summarize the published literature on dust mite control, it is apparent that benzyl benzoate and other miticidal compounds disclosed in the art can, under proper conditions of use, be effective in killing dust mites and thus helpful in reducing the level of allergens produced by said mites.

In any program aimed at controlling dust mites and their allergens, one of the steps should involve the laundering of clothing and other textile materials in which dust mites are present. Dust mites are killed at water temperatures of about 55°C and therefore, in theory at least, clothing and textile articles can be soaked in water at this temperature – without any detergent – and this will result in the elimination of dust mites. Although many domestic water

heating systems can attain a temperature of 55°C, such temperature is not recommended for many articles of clothing or fabrics, particularly those which are not colorfast at such high temperatures or which are made of synthetic materials. Furthermore, out of consideration for the environment and for economics, many consumers prefer to wash their clothes at temperatures ranging from room temperature up to about 40°C. The effect of water temperature in controlling dust mites is discussed in an article by Lindy G. McDonald and Euan Tovey, "The Role of Water Temperature and Laundry Procedures in Reducing House Dust Mite Populations and Allergen Content of Bedding", J. Allergy Clin. Immunol. 90:599-608 (1992).

Published European Patent Application No. 0,612,469 discloses laundry detergents comprising benzyl benzoate and various surfactants, which compositions are taught to be effective in killing dust mites at temperatures as low as 30°C.

Recently, there have been proposed a number of liquid detergent compositions which, in addition to the usual surfactants and other substances common to laundry detergents, also contain an effective amount of cationic surfactant germicides. Compositions of this type are finding general acceptance among consumers and it is expected that consumers also would welcome the opportunity to have a detergent product which, in addition to the usual function of laundering textiles and garments, provide germicidal properties and will kill a substantial number of dust mites. Although the incorporation of an acaricidal ingredient into a laundry detergent composition does not in itself amount to a full program of dust mite control, the use of such laundering compositions constitutes an important step in a program of dust mite control.

Liquid detergent compositions, particularly concentrated liquid detergent compositions which find particular use in laundering textiles and garments are well known to the art. Salient characteristics of such compositions include: good detergency, good anti-soil redeposition properties, minimal

deleterious effect to textiles or garments washed with the same, such as color fading or decomposition of the textile or garments due to the action of one or more constituents in the detergent compositions, i.e., undesirable enzymatic effects. Liquid detergent compositions of this type, which are well known to both commercial and private consumers, include detergent compositions which are marketed for use in the laundering of garments or textiles in a washing machine. While such compositions are well known to provide good cleaning effects, it is also known that such liquid detergent compositions, provide neither a particularly effective sanitizing or disinfecting effect to the laundered garments or textiles, nor any effectiveness in controlling dust mites. Accordingly, there exists a present need in the art of laundry detergent compositions for products which, at the same time provide (1) excellent detergency, (2) a sanitizing effect providing for a high level of protection against harmful bacteria as may normally be present in the household including Gram positive and Gram negative vegetative bacteria such as those belonging to the species: *Salmonella, Klebsiella* and *Staphylococcus*, and (3) effectiveness in killing common dust mites.

While such compositions would be desirable, these have also been difficult to readily produce as it is well known that certain quaternary ammonium compounds, which are known to be effective against such Gram positive and Gram negative vegetative bacteria, are cationic surfactants. Such germicides are not frequently found to be useful in detergent formulations, because many successful formulations comprise a significant fraction of one or more anionic surfactants, which are well known to be useful detersive agents but are considered incompatible with such cationic surfactants. Notwithstanding this technical problem, certain detergent formulations comprising cationic surfactant germicides are known.

For example, U.S. Patent No. 5,080,830 to Damaso teaches a water dispersible composition comprising a hydrophobic quaternary ammonium compound, a polyether derivative compound used as a dispersing agent and

certain quaternary ammonium salts which are used as a stabilizing agent for the aqueous formulations formed from these constituents.

U.S. Patent No. 5,368,756 to Vogel et al. provides a rinse added fabric softening composition which comprises a mixture of certain diester quaternary ammonium compounds with a highly ethoxylated hydrophobic material and a liquid carrier, preferably water. The invention appears to be directed to limiting the formation of soap scum caused by the interaction of the diester quaternary ammonium compound with anionic detergent surfactants and/or detergency builders which may be entrapped in a fabric being treated.

U.S. Patent No. 5,399,280 to Woo et al. provides certain hard surface detergent compositions comprising either a mixture of zwitterionic detergent surfactants or a low sudsing nonionic detergent surfactant with a suds reducing amount of a phosphorus containing alkoxylate, which compound provides good suds regulation and maintains good spotting/filming and rinsing characteristics, and optionally, but preferably, a hydrophobic solvent which itself provides additional cleaning activity.

U.S. Patent No. 5,409,621 to Ellis et al. teaches a fabric softening composition comprising a water insoluble quaternary ammonium compound and a nonionic stabilizing agent which may be an alkoxylated C_8-C_{22} linear alcohol comprising on average 10 or more moles of an alkylene oxide or which may be a C_{10}-C_{20} alcohol, or mixture thereof. These constituents are desirably provided in an aqueous carrier.

U.S. Patent No. 5,415,813 to Misselyn et al. provides an all-purpose liquid cleaner in the form of a microemulsion which finds use in cleaning hard surfaces and is said to be effective in removing grease soils. All of these compositions include a certain class of quaternary ammonium compounds; such compounds are cited as grease release agents.

U.S. Patent No. 4,576,729 to Paszek et al. provides stable liquid disinfectant laundry detergent compositions which comprise a nonionic

surfactant, a so-called cryptoanionic surfactant and a quaternary ammonium compound which is effective as a germicidal active agent, as well as minor amounts of other nonessential ingredients. Therein is taught that a critical combination of a nonionic surfactant of an ethoxylated octyl or nonyl phenol with a cryptoanionic surfactant of the alkyl alkoxy carboxylate class and a quaternary ammonium germicide in a water carrier in the particular ratios in the range of from 2:4:1 to 3.5:5:1, provide effective laundry detergent compositions which offer a germicidal effect and antisoil redeposition properties. The compositions are provided preferably in liquid form and may comprise other nonessential ingredients including foam stabilizers, anti-irritating agents, brighteners, fragrances, dyes, pH adjusters such as a buffer, or tri-ethanol amine and a viscosity modifier such as ethanol. It was observed that the nonionic ethoxylated octyl and/or nonyl phenol surfactants are an essential constituent in order to provide both stability and good detersive action. Further, as is illustrated on Table 2 of that patent, the compositions are effective as germicides in aqueous dilutions within the range of from 1:200 to 1:333 in parts by weight, with most of the compositions having germicidal efficacy at maximum dilutions of 1:200-250.

U.S. Patent No. 4,810,409 to Harrison et al. teaches compositions comprising a quaternary ammonium germicide, anionic and nonionic surfactants wherein the ratio of cationic:anionic surfactant is at least 3.3:1. The patentee demonstrates that such an excess of cationic surfactant is needed to maintain germicidal efficacy in the presence of the claimed amount of anionic surfactant.

U.S. Patent No. 4,493,773 to Cook et al. teaches certain low phosphate detergent compositions which include nonionic detergent surfactants, an alkyl polysaccharide detergent surfactant, and a cationic softening/anti-static compound which may be a quaternary ammonium salt. In the aforesaid compositions, the nonionic surfactant is preferably one according to the formula $R(OC_2H_4)_nOH$ wherein R is a primary C_{10-18} alkyl and n has an average value of from about 2 to 9. The alkyl polysaccharide detergent surfactant is one according

to the formula $RO(R'O)_y(Z)_x$: wherein R is an alkyl, hydroxalkyl, alkylphenol, hydroxyalkylphenol, alkylbenzyl or mixture of one or more of the above, and the alkyl groups comprise from 8 to 18 carbon atoms; R' contains from about 2 to 4 carbon atoms, y is a value from 0 to about 12, each Z is a moiety derived from reducing saccharide containing 5 or 6 carbon atoms, and x is a number from 1 to 10. The quaternary ammonium cationic surfactant has two chains which contain an average from about 16 to about 22 carbon atoms.

U.S. Patent No. 4,272,395 to Wright teaches a hard surface cleaning composition which comprises a quaternary ammonium compound as a germicidal active agent and a co-surfactant selected from the group consisting of: short chain anionic surfactants having C_3-C_8 in the hydrophobic group; low alkoxylated nonionic surfactants having from 0 to 4 ethylene oxide and/or propylene groups in the molecule, as well as mixtures thereof. Therein it is taught that compositions comprising a conventional anionic surfactant of more than 8 carbons in the hydrophobic group or conventional nonionic detergents having more than 4 ethylene oxide groups were found to be poor performers as compared with the short chain anionic surfactants of from 3 to 8 carbon atoms and/or low alkoxylated nonionic surfactants having from 0 to 4 ethylene oxide or propylene groups in the molecule. The compositions of the invention according to U.S. Patent 4,272,395 preferably comprise from 50 to 95 parts by weight of the quaternary ammonium, from 5 to 50 parts by weight of the anionic surfactant and from 0 to 20 parts by weight of the nonionic surfactant.

U.S. Patent No. 5,378,409 to Ofosu-Asante teaches a specific light duty liquid or gel dishwashing detergent composition which comprises a surfactant mixture (I) which includes: (a) 80-100% by weight of certain alkyl ethoxy carboxylates according to the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$, where R is C_{12}-C_{16} alkyl, x is 0 to 10 and M is a cation other than calcium, (b) from 0 to 10% by weight of alcohol ethoxylate according to the formula $RO(CH_2CH_2O)_xH$, where R is C_{12}-C_{16} alkyl and x is 0 to 10, and (c) from 0 to

10% of one or more soaps according to the formula $RCOO^-M^+$, where R is C_{11}-C_{15} alkyl and M is a cation; (II) from 0.1%-4% calcium ions; and (III) from 0 to about 10% of a calcium chelating agent said to prevent the formation of calcium carbonate precipitates in the composition, such that the said dishwashing detergent composition in a 10% by weight aqueous solution exhibits a pH of from 7 -11. The specification recites that the alkylethoxycarboxylate within the surfactant mixture does not comprise a calcium ion, and teaches the selected addition of certain salts in order to introduce the calcium ions in specific weight percentages. The presence of the calcium ions is cited as providing good grease removal, storage stability, and skin mildness. The specification also recites the use of limited amounts of certain cationic quaternary ammonium compounds as a suds boosting agent. Among the recited objects of the patent is to provide detergent compositions featuring good grease removal while simultaneously being mild to the skin, technical features which do not generally arise in laundry detergent compositions. Further, there is no mention in the specification of the use of such compositions in a laundry application, particularly a machine washing laundering application.

U.S. Patent No. 5,230,823 to Wise et al. teaches certain light duty or gel dishwashing detergent compositions which comprise from 5 to 70% by weight of a surfactant mixture comprising: (a) from 80 to 100% of an alkyl ethoxy carboxylate of the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$ wherein M^+ is a cation; (b) from 0-10% of alcohol ethoxylates according to the formula: $RO(CH_2CH_2O)_xH$; (c) 0-10% of a soap based upon the formula $RCOO^-M^+$, wherein a 10% by weight aqueous solution of the cleaning composition exhibits a pH of from 7-11. As opposed to U.S. Patent No. 5,378,409 discussed *supra*, U.S. Patent No. 5,230,823 teaches the utility of ions, including magnesium and calcium ions of which magnesium ions are particularly preferred. Also taught as an optional constituent are certain cationic quaternary ammonium surfactants as suds boosters, i.e., suds stabilizing surfactants. However, as in U.S. Patent No.

5,378,409, the recited objects of the U.S. Patent No. 5,230,823 include the provision of dishwashing detergent compositions featuring good grease removal while simultaneously being mild to the skin. Furthermore, there is no mention in the specification of the use of such compositions in a laundry application, particularly a machine washing laundering application.

U.S. Patent No. 4,364,457 to Beeks et al. discloses a cationic liquid laundry detergent and fabric softener comprising from 3 to 35% nonionic surfactant, from 3 to 30% quaternary ammonium surfactant, and a mixture of anionic surfactants selected from alkyl sulfates, alkyl ethersulfates and alkyl ethercarboxylates, in which the ratio of total cationic to total anionic surfactants is from 0.8:1 to 10:1. The specification makes no reference to any antibacterial properties for the composition.

U.S. Patent No. 4,333,862 to Smith et al. discloses a liquid detergent composition comprising from 2-100% of a surfactant system consisting essentially of a water soluble combination of anionic, nonionic and quaternary ammonium surfactants wherein the anionic:cationic ratio is less than 5:1 but at least 1:1 and the nonionic:cationic ratio is from 5:1 to 2:3. The specification makes no mention of any antibacterial properties.

U.S. Patents Nos. 5,151,223 to Maaser, 4,547,300 to Lareau and 4,233,167 to Sranek are all directed to compositions which include optical brighteners and which further include quaternary ammonium compounds as fabric softener additives.

Commonly assigned and copending patent application US 08/666897 describes liquid laundry detergent compositions which comprise: one or more anionic surfactant compositions selected from alkylethercarboxylates and alkylethersulfonates; at least one quaternary ammonium surfactant compositions having germicidal properties; one or more nonionic surfactant compositions selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides and alkanolamides; and optionally one or

more anionic co-surfactant compositions. While certain of the compositions described in that application include certain optical brighteners, as will be described and demonstrated in more detail hereinafter, such compositions according to U.S. 08/666897 are only poor to fair in their optical brightening characteristics, especially subsequent to repeated washings of garments.

While the above-described compositions provide certain advantageous features, the remains a real and continuing need in the art for improved liquid laundry detergent compositions which concurrently provide good detersive properties, an effective sanitizing benefit to laundered textiles and garments, excellent optical brightening characteristics especially after repeated washings, are also effective in killing dust mites. A multi-purpose laundry detergent with all of these features would be extremely advantageous.

Therefore, it is an object of the invention to provide improved laundry detergent compositions, more particularly to provide improved aqueous laundry detergent compositions in a concentrated form, which laundry detergent compositions provide good detersive and good sanitizing effects, kill dust mite at temperatures in the 20° to 40°C range, and which feature excellent optical brightening characteristics especially after repeated washings.

Summary of the Invention

According to the invention there is provided an aqueous, germicidal liquid detergent composition comprising:

A) a major anionic surfactant constituent selected from alkyl ether carboxylates and alkyl ether sulfonates;

B) a cationic germicidal surfactant;

C) a nonionic surfactant preferably selected from alcohol alkoxylates, alkylphenol alkoxylates, alkyl polyglycosides, amine oxides and alkanolamides

D) a compatible optical brightener constituent; and

E) an acaricidal compound effective against dust mites,

wherein the value of the cationic surfactant to the major anionic surfactant is 1:2 or greater.

The composition may optionally contain further anionic surfactants, provided that the weight ratio of the cationic to optional further anionic surfactants is critically maintained at a weight value of 2:1 and greater.

In accordance with preferred aspects of the present invention, there are provided aqueous germicidal liquid laundry detergent compositions in concentrated form, which compositions comprise water and the following constituents based on 100 parts of said compositions:

A) 2 - 20 parts by weight of one or more anionic surfactants selected from alkyl ether carboxylates and alkyl ether sulfonates;

B) 1-25 parts by weight of one or more quaternary ammonium surfactants having germicidal properties;

C) 2-40 parts by weight of one or more nonionic surfactants selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, and alkanolamides;

D) 0.001-1 parts by weight of a compatible optical brightener constituent;

E) 0.3 to 15 parts by weight of benzyl benzoate; and

F) 0 -10 parts by weight of one or more further anionic surfactants selected from alkyl sulfates, alkyl sulfonates, alkyl ether sulfates, alkylaryl sulfonates, alkylaryl ether sulfates, which are present in a proportion not to exceed one half of the weight of the one or more quaternary ammonium surfactants;

with the requirement that the weight ratio of B:A be 1:2 or greater.

Where the detergent compositions includes a further anionic surfactant

E, it is present in amounts where the weight ratio of B to E is 2:1, or greater.

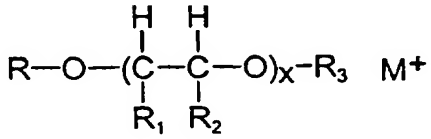
It is to be understood that the amounts of the named surfactants refers to the amount of actives in the respective surfactant preparation.

The compositions of the invention may further comprise optional constituents, many of which are well known to the art, including but are not limited to: detergency builders, chelating agents, pH adjusting agents, pH stabilizing agents (buffers), hydrotropes, optical brighteners, coloring agents, fragrances, fillers, as well as others not particularly elucidated here. These optional constituents may be added in any effective amount, but generally the total amount of such optional constituents does not exceed about 10 parts by weight of the total weight of the detergent compositions being taught herein.

Surfactants which find use in the present inventive compositions include materials which are known to the art and include those described in *McCutcheon's Detergents and Emulsifiers*, Vol. 1, North American Edition, 1991; as well as from *Kirk-Othmer, Encyclopedia of Chemical Technology,* 3rd Ed., Vol. 22, pp. 346-387, the contents of which are herein incorporated by reference. The conventional additives which may be further included as one or more of the optional constituents include materials which are also known to the art, and include materials described in the references noted above, as well as in *McCutcheon's Functional Materials* , Vol. 2, North American Edition, 1991

Constituent (A) Particularly useful anionic surfactants which find use in the detergent compositions according to the present invention include at least one alkylethercarboxylate surfactant, and/or at least one alkylethersulfonate surfactant.

Useful alkylethercarboxylate surfactants include compounds according to the formula:



where:

R is a C_4-C_{22} linear or branched alkyl group, preferably C_8-C_{15} linear or branched alkyl group, more preferably a C_{12-15} linear or branched alkyl group;

x is an integer from 1 to 24,

each of R_1, R_2 and R_3 is a group selected from H, lower alkyl radicals including methyl and ethyl radicals, carboxylate radicals including acetate and propionate radicals, succinate radicals, hydroxysuccinate radicals, or mixtures thereof wherein at least one R_1, R_2 or R_3 is a carboxylate, succinate or hydroxysuccinate radical; and,

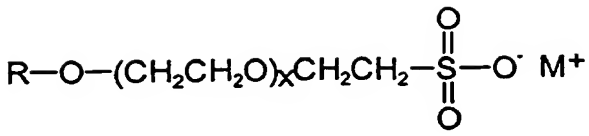
M^+ is a counterion including an alkali metal or ammonium ion.

Free acid forms of these alkyl ether carboxylate compounds may also be used. Preferably, the alkyl ether carboxylate compound is one wherein R is C_{12}-C_{15}, x is an integer from 1 to 10, and R_1, R_2, and R_3, which may be the same or different, are preferably selected from H and carboxylate radicals. Most preferred are alkylethercarboxylate compounds wherein R is C_{12}-C_{15}, x is an integer from 1 to 10, R_1 and R_2 are both hydrogen, and R_3 is a CH_2COO^- radical, M^+ is a counterion selected from sodium, potassium and ammonium ions.

Such alkyl ether carboxylate compounds are per se known and are available in commercial preparations wherein they are frequently provided in an aqueous carrier. Examples of such currently available commercial preparations include SURFINE WLG (Finetex Inc., Elmwood Park NJ) and SANDOPAN DTC (Clariant Chem.Co., Charlotte NC) in salt forms, NEODOX (Shell Chemical Co., Houston TX) in free acid form.

Alternatively, or in addition to the alkylethercarboxylate surfactants noted above, there may be used one or more alkylethersulfonate surfactants.

Exemplary alkyl ether sulfonate surfactants include those according to the formula:



where:

R is a C_4-C_{22} linear or branched alkyl group, preferably C_8-C_{15} linear or branched alkyl group, and more preferably a C_{12-15} linear or branched alkyl group;

x is an integer from 1 to 24; and

M^+ is alkali metal or ammonium counterion.

Free acid forms of these alkyl ether sulfonate compounds may also be used. Preferably, the alkyl ether sulfonate compound is one wherein R is C_{12}-C_{15}, x is from 1 to 10 and M^+ is a counterion selected from sodium, potassium and ammonium ions.

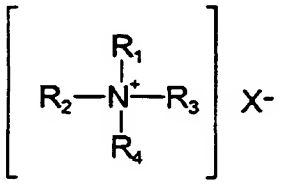
Such alkyl ether sulfonate compounds are known and are available in commercial preparations wherein they are frequently provided in an aqueous carrier. Examples of such commercially available preparations include AVANEL S30 and AVANEL S70 (PPG Industries, Pittsburgh PA)

In the concentrated liquid detergent compositions according to the invention, the anionic surfactant of Constituent (A) comprises from 1 to 40 parts by weight of the liquid detergent compositions, more preferably from 5 to 30 parts by weight of the active constituents of the liquid detergent compositions, but most preferably comprise from 10 to 20 parts by weight of the liquid detergent compositions.

According to particularly preferred embodiments, the anionic surfactant constituent (A) consists solely of an alkylethercarboxylate or an alkylethersulfonate surfactant.

Constituent (B) Cationic surfactants which exhibit germicidal activity and which may be used in the detergent compositions include certain quaternary ammonium surfactants, of which one or more such cationic surfactants may be

used as the present Constituent (B). Particularly useful quaternary ammonium compounds and salts thereof include quaternary ammonium germicides which may be characterized by the general structural formula:

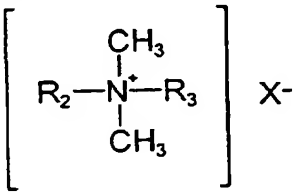


where at least one of R_1, R_2, R_3 and R_4 is a hydrophobic aliphatic, arylaliphatic or aliphaticaryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxyaryl, long-chain alkylaryl, halogen-substituted long-chain alkylaryl, long-chain alkylphenoxyalkyl, arylalkyl, etc. The remaining radicals on the nitrogen atom other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms. The radicals R_1, R_2, R_3 and R_4 may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ester linkages. The radical X may be any salt-forming anionic radical.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyltrimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyldimethylbenzylammonium bromide, N-alkyl pyridinium halides such as N-cetylpyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide or ester linkages such as octylphenoxyethoxyethyldimethylbenzyl ammonium chloride, N-(laurylcocoaminoformylmethyl)-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminophenyltrimethylammonium methosulfate,

dodecylphenyltrimethylammonium methosulfate, dodecylbenzyltrimethylammonium chloride, chlorinated dodecylbenzyltrimethylammonium chloride, and the like.

Preferred quaternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:



wherein R_2 and R_3 are the same or different C_8-C_{12}alkyl groups, or R_2 is C_{12}-$_{16}$alkyl, C_{8-18}alkylethoxy, C_{8-18}alkylphenolethoxy and R_3 is benzyl, and X is a halide, for example chloride, bromide or iodide, or methosulfate. The alkyl groups recited in R_2 and R_3 may be straight chained or branched, but are preferably substantially linear.

Particularly useful quaternary germicides include compositions which include a single quaternary compound, as well as mixtures of two or more different quaternary compounds. Particularly useful quaternary germicides include: BARDAC® 205M, and BARDAC® 208M or BTC® 885which is described to be a blend of alkyldimethylbenzyl ammonium chlorides; BARDAC® 2050 and BARDAC® 2080 or BTC® 818 which is described to be based on dialkyl(C_8-C_{10})dimethylammonium chloride; BARDAC® 2250 and BARDAC® 2280 or BTC® 1010 which is described to a composition which includes didecyldimethylammonium chloride; BARDAC® LF and BARDAC® LF 80 which is described to be based on dioctyldimethylammonium chloride; BARQUAT® MB-50, HYAMINE® 3500, BARQUAT® MB-80, BTC® 835 or BTC 8358 each described to be based on alkyldimethylbenzylammonium chloride; BARQUAT® MX-50, BARQUAT® MX-80, BTC® 824 or BTC®

8248 each described to be a composition based on alkyldimethylbenzylammonium chloride; BARQUAT® OJ-50, BARQUAT® OJ-80, BTC® 2565, or BTC® 2658 each described to be a composition based on alkyldimethylbenzylammonium chloride; BARQUAT® 4250, BARQUAT® 4280, BARQUAT® 4250Z, BARQUAT® 4280Z, BTC® 2125, or BTC® 2125M each described to be a composition based on alkyldimethylbenzylammonium chloride and/or alkyl dimethylethylbenzylammonium chloride; BARQUAT® MS-100 or BTC® 324-P-100 each described to be based on myristyldimethylbenzylammonium chloride; HYAMINE® 2389 described to be based on methyldodecylbenzylammonium chloride and/or methyldodecylxylene-bis-trimethylammonium chloride; HYAMINE® 1622 described to be an aqueous solution of benzethonium chloride; HYAMINE® 3500-NF or BTC® 50 each described to be based on alkyldimethylbenzylammonium chloride; as well as BARQUAT® 1552 or BTC® 776 described to be based on alkyldimethylbenzylammonium chloride and/or dialkylmethylbenzylammonium chloride. (Each of these recited materials is currently commercially available from Lonza, Inc., Fairlawn, NJ and/or from Stepan Co., Northfield IL)

In the liquid laundry detergent compositions according to the invention Constituent (B) comprises from 1 to 25 parts by weight of the active constituents of the detergent compositions, more preferably comprise from 2 to 20 parts by weight, and most preferably comprise from 3 to 7 parts by weight of the active constituents of the liquid detergent compositions.

It has been surprisingly found that especially effective germicidal efficacy of the detergent composition, when diluted to form a wash bath as indicated in more detail below, is attained when the weight ratios of such actives of Constituent (B):Constituent (A) is at least 1:2 or greater, such as for example 1.5:2, 2:2, 2.5:2 and even higher.

Constituent (C) The compositions according to the present invention further comprise one or more nonionic surfactants selected from surfactants based upon linear and secondary alcohols, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, and, alkanolamides. Such nonionic surfactants are known and are available in commercial preparations, certain such commercial preparations providing the surfactant compound in conjunction with an aqueous carrier.

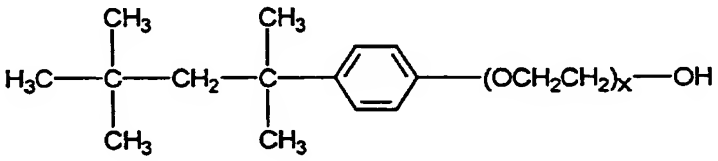
Useful nonionic surfactants include the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide, tridecanol condensed with about 6 to moles of ethylene oxide, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with a distillation fraction of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to about 14 carbon atoms in length and wherein the condensate contains either about 6 moles of ethylene oxide per mole of total alcohol or about 9 moles of ethylene oxide per mole of alcohol, and tallow alcohol ethoxylates containing from 6 to 11 moles of ethylene oxide to 11 ethylene oxide per mole of alcohol.

A preferred group of nonionic surfactants are those which are presently being marketed under the trade name, NEODOL (Shell Chemical. Co., Houston TX) These nonionic surface active agents are believed to be ethoxylated higher aliphatic, primary alcohols containing about 9-15 carbon atoms, such as C_9-C_{11} alkanol condensed with 8 moles of ethylene oxide (NEODOL 91-8), C_{12-13} alkanol condensed with 6.5 moles ethylene oxide (NEODOL 23-6.5), C_{12-15} alkanol condensed with 12 moles ethylene oxide (NEODOL 25-12), C_{14-15} alkanol condensed with 13 moles ethylene oxide (NEODOL 45-13), and the like.

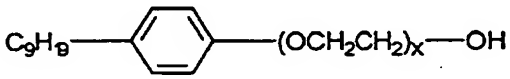
Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol

containing from 8 to 18 carbon atoms in a straight or branched chain configuration condensed with from 5 to 30 moles of ethylene oxide. Such nonionic surfactants are presently commercially available under the trade name TERGITOL (Union Carbide Corp., Danbury, CT). Specific examples of such commercially available nonionic surfactants of the foregoing type are C_{11}-C_{15} secondary alkanols condensed with either 9 moles ethylene oxide (TERGITOL 15-S-9) or 12 moles ethylene oxide (TERGITOL 15-S-12).

Other suitable nonionic surfactants include the polyethylene oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight- or branched chain alkyl group with from about 5 to 30 moles of ethylene oxide. Specific examples of alkylphenol ethoxylates include nonylphenol condensed with about 9.5 moles of ethylene oxide per mole of phenol, dinonylphenol condensed with about 12 moles of ethylene oxide per mole of phenol, dinonylphenol condensed with about 15 moles of ethylene oxide per mole of phenol, and diisoctylphenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include IGEPAL CO-630, a nonylphenol ethoxylate marketed by ISP Corp. (Wayne, NJ). Further exemplary commercially available nonionic surfactants include ethoxylated octyl and nonyl phenols having one of the following general structural formulas:



or,



in which the C_9H_{19} group in the latter formula is a mixture of branched chained isomers, and x indicates an average number of ethoxy units in the side chain. Suitable non-ionic ethoxylated octyl and nonyl phenols include those having

from about 7 to about 13 ethoxy units. Such compounds are commercially available under the trade name TRITON® X (Union Carbide Corp., Danbury CT).

Alkyl polyglycosides may also be used as a nonionic surfactant in the present inventive compositions. Suitable alkyl polyglycosides are known nonionic surfactants which are alkaline and electrolyte stable. Alkyl mono and polyglycosides are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide, with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside compounds including alkoxylated glycosides and processes for making them are disclosed in U.S. Patent No. 2,974,134, U.S. Patent No.3,219,656, U.S. Patent No. 3,598,865, U.S. Patent No. 3,640,998, U.S. Patent No. 3,707,535, U.S. Patent No. 3,772,269, U.S. Patent No. 3,839,318, U.S. Patent No. 3,974,138, U.S. Patent No. 4,223,129 and U.S. Patent No. 4,528,106.

A preferred group of alkyl glycoside surfactants suitable for use in the practice of this invention is represented by the formula:

$$RO\text{---}(R_1O)_y\text{---}(G)_xZ_b \qquad \text{I}$$

wherein:

R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to about 18, carbon atoms;

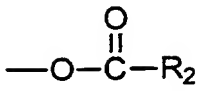
R_1 is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms;

y is a number which has an average value from about 0 to about 1 and is preferably 0;

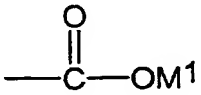
G is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; and

x is a number having an average value from about 1 to 5 (preferably from 1.1 to 2);

Z is O_2M^1,



$O(CH_2)$, CO_2M^1, OSO_3M^1, or $O(CH_2)SO_3M^1$ where R_2 is $(CH_2)CO_2M^1$ or $CH=CHCO_2M^1$ and M^1 is H^+ or an organic or inorganic cation, such as, for example, an alkali metal, ammonium, monoethanolamine, or calcium, with the proviso that Z can be O_2M^1 only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom, —CH_2OH, is oxidized to form a



group; and

b is a number of from 0 to 3x+1 preferably an average of from 0.5 to 2, per glycosal group;

R is generally the residue of a fatty alcohol having from about 8 to 30, and preferably 8 to 18, carbon atoms. Preferred alkyl polyglycosides include: APG™ 325 CS GLYCOSIDE which is described as being a 50% C_9-C_{11} alkyl polyglycoside, also commonly referred to as D-glucopyranoside; and GLUCOPON™ 625 CS which is described as being a 50% C_{10}-C_{16} alkyl polyglycoside, also commonly referred to as a D-glucopyranoside, (both commercially available from Henkel Corp., Ambler PA).

Also useful in the nonionic surfactant constituent of the invention are nonionic surfactant compositions based on amine oxides.

One general class of useful amine oxides include alkyl di (lower alkyl) amine oxides in which the alkyl group has about 10-20, preferably 12-16, carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups have between 1 and 7 carbon atoms. Examples include lauryldimethylamine oxide, myristyldimethylamine oxide, and those in which the alkyl group is a mixture of different amine oxides such as dimethylcocoamine

oxide, dimethyl(hydrogenated tallow)amine oxide, and myristyl/palmityldimethylamine oxide.

A further class of useful amine oxides include alkyl di (hydroxy lower alkyl) amine oxides in which the alkyl group has about 10-20, preferably 12-16, carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are bis(2-hydroxyethyl) cocoamine oxide, bis(2-hydroxyethyl) tallow amine oxide, and bis(2-hydroxyethyl) stearylamine oxide.

Further useful amine oxides include those which may be characterized as alkylamidopropyl di(lower alkyl) amine oxides in which the alkyl group has about 10-20, preferably 12-16, carbon atoms, and can be straight or branched chain, saturated or unsaturated. Examples are cocoamidopropyldimethylamine oxide and tallowamidopropyldimethylamineoxide; and

Additional useful amine oxides include those which may be referred to as alkylmorpholine oxides in which the alkyl group has about 10-20, preferably 12-16, carbon atoms, and can be straight or branched chain, saturated or unsaturated.

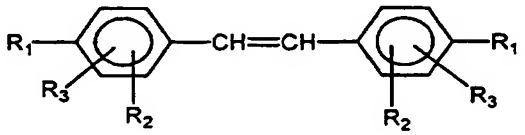
Further examples of such useful include nonionic surfactant compositions based on amine oxides include those which are presently commercially available and include those under the trade name AMMONYX (Stepan Co., Chicago IL).

In the concentrated liquid detergent compositions according to the invention Constituent (C) comprises from 3 to 50 parts by weight of the active constituents in the detergent compositions taught herein. More preferably, the nonionic surfactant composition comprises from 5 to 30 parts by weight, and most preferably from 10 - 25 parts by weight, of the active constituent of the present inventive liquid detergent compositions.

Constituent (D) The compositions according to the invention further include an effective amount of at least one compatible optical brightener constituent.

Whereas the prior art is replete with references to the use of such optical brightener constituents in laundry detergent applications, the prior art fails to take into consideration the production of a germicidal liquid laundry detergent composition which on the one hand provides effective germicidal action to garments being laundered and at the same time, provides good wash and appearance characteristics to laundered articles and textiles, especially light colored articles and textiles, inter alia, white. In contrast to many prior art liquid laundry detergent composition, the presence of the cationic germicidal quaternary surfactant of Constituent (B) has been found to render most stilbene based optical brighteners incompatible in formulations as such optical brighteners are very frequently highly anionic in nature and form complexes with cationic compounds, and thereby deactivate the activity of both themselves and the cationic compounds. In germicidal liquid laundry detergent compositions such as those taught herein, the inventor has found that the simple addition of optical brightener constituents complexes with the germicidal quaternary ammonium compound and undesirably deactivates both the germicidal activity and the optical brightening characteristics of the detergent compositions. Thus, the formulation of a successful germicidal liquid laundry detergent composition is not an obvious or trivial exercise for one skilled in the art, and is further complicated by the need to avoid attenuating the acaricidal activity of the ingredient added for the purpose of killing dust mites.

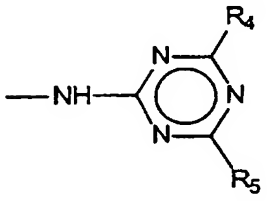
Exemplary stilbene based optical brighteners include those which may be represented by the general structure:



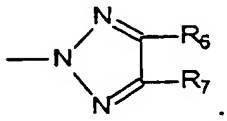
wherein:

each R_1 may be the same or different and are selected from substituted and unsubstituted groups including but not limited to hydrogen, alkyl especially

lower alkyl, benzyl, alkoxy, especially lower alkoxy such as ethoxy and propoxy, hydroxy, $-SO_3H$,



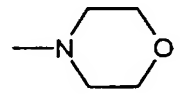
and



;

each R_2 and R_3 which may be the same or different, is selected from hydrogen, alkyl especially lower alkyl, benzyl, alkoxy, especially lower alkoxy such as ethoxy and propoxy, hydroxy, $-SO_3H$, halo, CN, alkyl sulfonyl, or esters such -COO-alkyl or -COO-aryl the alkyl or aryl groups of which esters may be optionally substituted, but most desirably R_2 and R_3 is hydrogen or $-SO_3H$;

each R_4 and R_5 which may be the same or different, may be any of a variety of substituted and unsubstituted groups including but not limited to hydrogen, alkyl, benzyl, alkoxy, hydroxy, $-NHC_6H_5$, $-OCH_3$, $-SO_3H$,



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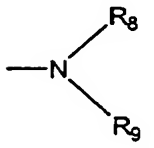

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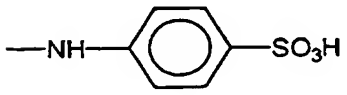

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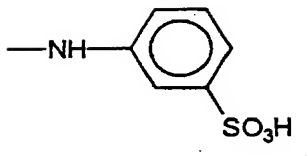
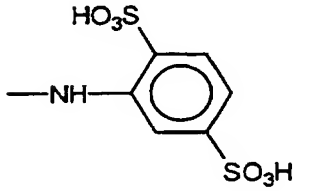


and



as well as other substituent groups, which may be unsubstituted or optionally substituted;

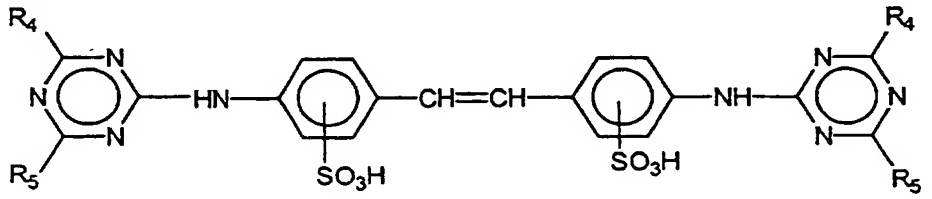
each R_6 and R_7, which may be the same or different, may be substituted and unsubstituted groups including but not limited to halo, lower alkyl, lower alkoxy, -CN,

-COOH, esters such -COO-alkyl or -COO-aryl, or which may together form a 4-, 5- or 6- membered ring; and,

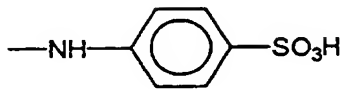
each R_8 and R_9 which may be the same or different, is selected from hydrogen, lower alkyl, especially C_1-C_6 and more especially C_1-C_3, hydroxy, and alkoxy especially ethoxy, propoxy or butoxy.

By way of illustration, but not limitation, groups useful in as substituent groups denoted above include halo, amino, lower alkyl, and lower alkoxy.

Preferred stilbene based optical brighteners are typically the symmetric or asymmetric derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid which may be generally represented as:



wherein R_4 and R_5 are as described above, but are preferably selected from:



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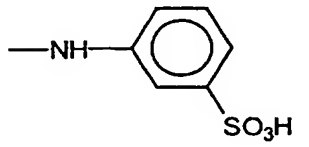

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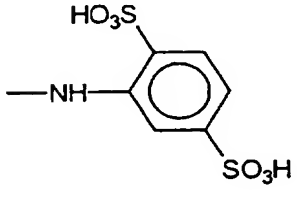
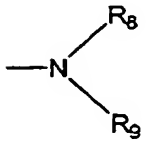


and,



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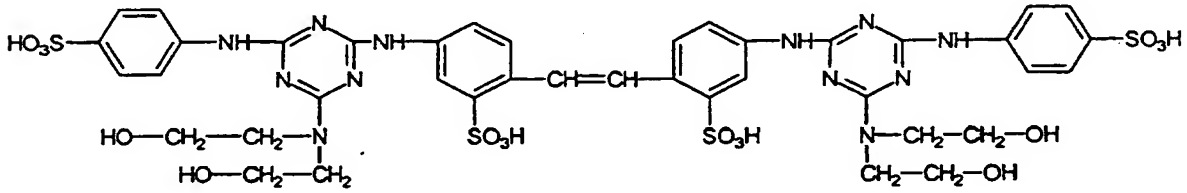
as defined above.

Further exemplary stilbene based optical brighteners are described in U.S. Patent No. 3,761,470, the contents of which are herein incorporated by reference.

Various materials of the classes described above may be obtained from a variety of commercial sources including but not limited to products currently marketed under the trade names Phorwite® which are marketed for whitening of paper and Blancophor® especially Blancophor® TX which is marketed for whitening of textile and laundry (Bayer Corp., Pittsburgh, PA and Bayer AG, Leverkusen, Germany); Leucophor® (Clariant Corporation, Charlotte NC and Clariant AG, Muttenz, Switzerland), Tinopal® (Ciba-Specialty Chemicals, Greensboro, NC). Such products are usually provided in an aqueous carrier medium, and may be provided in free acid form, or in a salt forms of their corresponding acids, i.e., sodium, potassium, or other alkali metal or alkaline earth metal salts.

It has been discovered that the stilbene based optical brighteners having three or more sulfate groups and/or sulfonic acid groups per molecule forming part of the germicidal liquid laundry detergent compositions taught herein provide the benefit of excellent optical brightening and apparent whitening of laundered garments or textiles, and at the same time do not complex or react with the germicidal quaternary ammonium compounds or with the acaricidal ingredient such to deleteriously affect the sanitizing and acaricidal properties of the laundry detergent compositions.

An exemplary particularly preferred compatible optical brightener is a compound according to:



Such is presently available in a commercial preparation as PHORWITE® P-150 from the Bayer Corp.(Pittsburgh, PA), and includes four sulfur containing groups.

While the compatible optical brightener constituent may be used in any effective amount, typically at least 0.001%wt., desirably it forms not more than about 1%wt. of the compositions according to the invention. Still more desirably, the compatible optical brightener constituent forms from 0.2 – 0.8 %wt. of the inventive composition, and most desirably is present in amounts of from 0.25 – 0.5 %wt., each of these weights being based on the amount of actives in the commercially supplied optical brightener preparation.

Constituent (E) While a number of acaricidal compounds such as those disclosed in U.S. Patent No. 4,800,196 (discussed above) have exhibited some effectiveness in killing dust mites, the preferred compound for use in connection with this invention is benzyl benzoate. This compound is particularly effective, is non-toxic and, when used in the amount specified herein, causes no

environmental damage. Benzyl benzoate is available from various sources, including particularly, Sigma Chemical Company (St. Louis, MO), and Morflex Inc. (_____, __).

Although benzyl benzoate has been previously reported as being effective in laundry detergent compositions for the killing of dust mites, it has been found that detergent compositions containing both benzyl benzoate and a quaternary ammonium compound of Constituent (B) are particularly effective in killing dust mites. This apparently synergistic response is quite surprising since the quaternary ammonium compounds themselves are of limited effectiveness against dust mites.

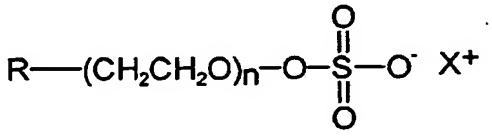
Benzyl benzoate should be present in the detergent compositions of this invention in amounts ranging from about 0.3 weight percent to about 15 weight percent, preferably from 0.5 to 10 weight percent.

Constituent (F) While not always included in compositions according to the present invention, it has been found that a minor amount of a further anionic co-surfactant provides further detersive action and foaming action. Such further anionic surfactant is present in a relatively small amount, i.e., less than 10 parts by weight based on the total weight of the liquid detergent composition, with the further limitation that such anionic co-surfactant is present in an amount of no more than ½ of the total weight of Constituent (B).

Anionic surfactants which are useful for use as the recited anionic co-surfactant may be any anionic surfactant which is determined not to undesirably detract from the efficacy of Constituent (B) when included in a formulation within the scope of the instant invention. Known anionic surfactants may be used, including for example, alkali metal salts or ammonium salts of compounds selected from certain alkylsulfates, alkylsulfonates, alkylethersulfates, alkylarylsulfonates, alkylarylethersulfates, and mixtures thereof.

One class of useful anionic surfactants as the co-surfactant herein

includes alkyl ethersulfates and salts thereof, especially one or more alkyl ethersulfates which may be represented by the following general formula:



wherein R is a C_8 - C_{18} alkyl group, n is an integer from 1 to 30, and X represents an counterion selected from alkali metals and ammonium. Of these alkyl ethersulfates, especially preferred are those wherein R is a C_{12}-C_{15} group, n is 4, and X is a sodium cation or is an ammonium cation. Such alkyl ether sulfates may be produced by known methods, or in the alternative are commercially available under the trade name STEOL (Stepan Co., Northbrook, IL).

Other anionic surfactants which may be present as co-surfactants include one or more alkyl sulfates, alkyl sulfonates, alkylaryl sulfonates or alkylaryl ether sulfates, all of which types are well known in the art.

As indicated above, when present, the anionic co-surfactant according to Constituent (F) comprises from 0 to 10 parts by weight of the liquid detergent compositions of the present invention. More preferably the anionic co-surfactant comprises from 1 to 8 parts by weight, and most preferably from 2 to 5 parts by weight, of the liquid detergent compositions. However, the weight ratio of the cationic Constituent (B) to the anionic co-surfactant composition of Constituent (F) is at least 2:1; preferably the ratio is greater, i.e., at least 2.5:1.

Other Constituents Optionally, the compositions include up to 10% by weight of conventional laundry detergent additives as known in the art including but not limited to: builders, chelating agents; pH adjusters; stabilizers; rheology modifying agents; sequestrants; solvents including alcohols such as ethanol and propylene glycol; hydrotropes such as sodium and potassium aryl sulfones and alkylaryl sulfonates, coloring agents, and fragrances. Many of these are known to the art, and include those which are described in *McCutcheon's Functional Materials*, Vol.2, North American Edition, (1991). Each may be included at

effective concentrations, with the total of such optional constituents preferably not exceeding 10% by weight of the total liquid laundry detergent composition taught herein.

For the stabilization of the inventive composition pH stabilizing agents (also referred to as pH buffers) is compatible with the aqueous compositions taught herein may be used. Examples of such useful pH buffer compounds and/or pH buffering systems or compositions include alkali metal and ammonium phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain other salts, such as the alkaline earth phosphates, carbonates and hydroxides, can also function as buffers. It may also be suitable to use as buffer materials such as aluminosilicates (zeolites), borates, aluminates and certain organic materials such as gluconates, succinates, maleates, and their alkali metal salts. Such buffers keep the pH ranges of the compositions of the present invention within acceptable limits. Other pH buffers, not particularly elucidated here may also be used. Preferably, citric acid, which is available as an anhydrous salt of an alkali metal citric acid, may be added as it is readily commercially available, and effective.

As noted above, the compositions of the invention when diluted to form a 0.20% solution in water (which is equivalent to a dilution of 1 part of the inventive composition to 500 parts water, preferably deionized water) exhibit a pH in the range of 5-10, more preferably a pH in the range of 7-8, and most preferably about 8. The incorporation of an effective amount of a pH stabilizing agent provides the technical benefits of ensuring the stability of the compositions of the invention as formulated and, when added to an excess of water, to form a cleaning composition therefrom. As is known to those skilled in the relevant art, various stains and food deposits may impart an appreciable change in the pH of water from an approximately neutral pH to that of an acidic or basic pH. The inclusion of an effective amount of a pH stabilizing agent in the compositions,

when added to the excess of water, will tend to return the pH of to cleaning composition to a more neutral level. While it will be realized that the selection of the other constituents forming the inventive compositions may necessitate varying amounts of a pH buffer composition, the buffer composition generally is included in effective amounts which are conventionally determinable in order to adjust the pH of the diluted compositions to the indicated pH ranges, particularly to the preferred pH ranges indicated above.

A further optional constituent which may be desirably included in the inventive compositions is a detergency builder component. Detergency builders, of the organic or inorganic type may be included in the present inventive compositions. Exemplary builders include water soluble inorganic builders which can be used alone or in admixture with other water soluble inorganic builders, as well as in conjunction with one or more organic alkaline sequestrant builder salts. When present, the detergency builder component generally is included to comprise up to 6 parts by weight, but preferably only up to 5 parts, of the composition.

Exemplary detergency builders include alkali metal carbonates, phosphates, polyphosphates and silicates. More specific examples include sodium tripolyphosphate, sodium carbonate, potassium carbonate, sodium polyphosphate, potassium pyrophosphate, potassium tripolyphosphate, and sodium hexametaphosphate.

Exemplary organic alkaline sequestrant builder salts include alkali and alkaline earth metal polycarboxylates including water-soluble calcium, sodium and potassium citrates, tartrates, ethylenediaminetetraacetates, N-(2-hydroxyethyl)-ethylenediaminetriacetates, nitrilotriacetates, and mono- or di-succinates. As noted, these organic builder salts may be used individually, as a combination of two or more organic builder salts, as well as in conjunction with one or more detergency builders, including those indicated above. Of these, especially preferred are ethylenediaminetetraacetic acid and salts thereof,

particularly calcium and sodium salts, and HEDTA and salts thereof. Other known chelating agents may be used, including sodium gluconate, gluconic acid and salts thereof, and sorbitol.

Further optional, but frequently desirable constituents include fragrances, which may be derived from natural sources or which may be synthetically produced. Such fragrances are known to the art, and may be added in any conventional manner, such as by admixing to a concentrate composition or blending with other constituents used to form a concentrate composition, in amounts which are found to be useful to enhance or impart the desired scent characteristic to the concentrate composition, and/or to cleaning compositions formed therefrom.

Further optional, but advantageously included, constituents are one or more coloring agents which find use in enhancing the appearance of the concentrate compositions and from the perspective of a consumer or other end user. Known coloring agents may be incorporated in the compositions in any effective amount to improve or impart to concentrate compositions a desired appearance or color. Such coloring agents may be added in a conventional fashion, i.e., admixing to a concentrate composition or blending with other constituents used to form a concentrate composition.

Water forms a constituent of the concentrated liquid detergent compositions. The water may be tap water, but is preferably distilled and/or deionized water. If the water is tap water, it is preferably appropriately filtered in order to remove any undesirable impurities such as organics or inorganics, especially mineral salts which are present in hard water which may thus interfere with the effectiveness of the composition. The amount of water added is an amount to provide the balance of the composition to provide 100 parts by weight. Generally, the water is added, generally in an amount of 40 to 95 parts by weight, so to provide the balance of the total inventive composition. It is to be recognized that one or more of the constituents according to the invention may be

commercially available as aqueous mixtures comprising one or more actives constituents, in which case their aqueous portion is to be considered separately from the actives portion, as has been noted above. Also, as has been previously noted, up to 10 parts by weight of the total liquid laundry detergent composition may be comprised of the one or more optional conventional laundry detergent additives and accordingly, the total amount of water must be proportionately reduced to allow the addition of such further optional additives.

In addition to their sanitizing and acaricidal properties, the compositions according to the present invention are particularly useful as an aqueous liquid detergent in concentrated form. The critical detersive components of the composition are the predominant anionic surfactants of Constituent (A), viz., the alkylethercarboxylate, and/or alkylethersulfonate, and Constituent (C), viz., the one or more quaternary ammonium surfactants. We have surprisingly discovered that the critically selected anionic surfactants are compatible with quaternary ammonium germicides in the recited proportions. Thus, up to very high ratios of anionic surfactant to cationic quaternary ammonium surfactant are now obtainable in accordance with the present inventive teaching, as compared with prior art teachings relating to the compatibility between anionic and cationic surfactants. By compatibility, it is meant that these critically selected anionic surfactants do not impair the antimicrobial activity of the quaternary component to any significant degree. This is in sharp contrast to other anionic surfactants, which significantly impair the antibacterial activity of quaternaries, as has been recited in the prior art and exemplified below. The surprising discovery described in the instant invention allows the formulation of unique and useful detergent compositions which simultaneously provides excellent cleaning combined with uncompromised antibacterial protection, even in formulations with high levels of anionic surfactant.

The compositions according to the invention are prepared by dissolving the individual constituents in order to provide a liquid concentrate.

The order of adding the various ingredients is not of major importance, but the person skilled in the art will realize that benzyl benzoate is insoluble in water and will take this fact into consideration when preparing the subject concentrates. In use, the concentrate is added to the wash water in an amount effective to achieve cleaning and brightening effects as well as sanitization of the fabrics or garments being washed and elimination of dust mites present in or on the treated fabrics and garments. It has been found that from approximately 120 to about 180 ml. of the liquid laundry detergent concentrate compositions per wash load (domestic washing machine) is generally adequate to achieve the desired results in a domestic wash load. Thus, based on the total wash water volume of approximately 60 litres of water, the compositions can be used at dilutions of the concentrated composition:water from about 1:500 to about 1:330, although even lower dilutions may be also used and provide such excellent cleaning, sanitization and acaricidal effects. Conventional washing machines may be used utilizing conventional washing cycles, particularly wherein the wash water is at a temperature in the range of 20°C - 40°C degrees, and for a bath contact time of 10-20 minutes.

This invention will be better understood by reference to the following examples which are included here for purposes of illustration and no limitation.

Example 1

A formulation was prepared by adding the measured amount of deionized water to a glass beaker. Using a magnetic stirrer, the water was stirred during the addition of further measured amounts of the remaining constituents. After all of the constituents had been stirred in, the formulation was stirred for a further 30 minutes using a magnetic stirring bar. The resulting formulation was a homogeneous liquid, suitable for use as a laundry detergent at a dilution rate of about 1:500 in a household washing machine. The following table shows the

constituents of this formulation:

INGREDIENT:	TRADE NAME:	SUPPLIER:	PERCENT BY WEIGHT:
Alcohol Ethoxy Carboxylate 95%	Neodox 25-6	Shell	7.24
Linear Primary Alcohol Ethoxylate 100%	Neodol 25-7	Shell	10
Water, deionized	--	--	q.s.
Sodium Hydroxide, 50%	Sodium Hydroxide	Fisher	1
Stilbene disulfonic acid derivative 28%	Phorwite P150	Bayer	1.79
Dioctyl Dimethyl Ammonium Chloride, 50%	Bardac LF	Lonza	7.5-12.5
Benzyl Benzoate 100%	Benzyl Benzoate	Morflex Inc.	3

CLAIMS:

1. An aqueous, germicidal and acaricidal liquid detergent composition comprising:

A) a major anionic surfactant constituent selected from alkyl ether carboxylates and alkyl ether sulfonates;

B) a cationic germicidal surfactant;

C) a nonionic surfactant selected from alcohol alkoxylates, alkylphenol alkoxylates, alkyl polyglycosides, amine oxides and alkanolomides;

D) a compatible optical brightener constituent; and

wherein the weight ratio of the cationic surfactant to the major anionic surfactant is 1:2 or greater.

2. A detergent composition according to claim 1 comprising:

A) 2 - 20 parts by weight of one or more anionic surfactants selected from alkyl ether carboxylates and alkyl ether sulfonate;

B) 1-25 parts by weight of one or more quaternary ammonium surfactant having germicidal properties;

C) 2-40 parts by weight of one or more nonionic surfactant selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, and alkanolamides;

D) 0.001-1 parts by weight of a compatible optical brightener constituent;

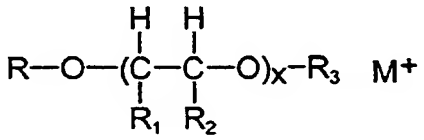
E) 0.3-15 parts by weight of benzyl benzoate; and

F) 0 -10 parts by weight of one or more further anionic surfactants selected from alkyl sulfates, alkyl sulfonates, alkyl ether sulfates, alkylaryl sulfonates, and alkylaryl ether sulfates which are present in a proportion not to exceed one half of the weight of the one or more quaternary ammonium surfactants;

wherein the weight ratio of B:A is 1:2 or greater.

3. A detergent composition according to claim 2 wherein the major anionic surfactant constituent (A) consists solely of an alkyl ether carboxylate.

4. A detergent composition according to claim 3 wherein the anionic surfactant has the formula:



where:

R is a C_{4-22} linear or branched alkyl group,

x is an integer from 1 to 24,

each of R_1, R_2 and R_3 is a group selected from H, lower alkyl radicals including methyl and ethyl, carboxylate radicals including acetate and propionate, succinate radicals, hydroxysuccinate radicals, and at least one R_1, R_2 and R_3 is a carboxylate, succinate or hydroxysuccinate radical, and

M^+ is alkali metal or ammonium counterion.

5. A detergent composition according to claim 4 wherein:

R is a C_{12-15} linear or branched alkyl group,

x is an integer from 1 to 10, and

each of R_1, R_2 and R_3 is a group selected from H and carboxylate radicals, and at least one R_1, R_2 and R_3 is a carboxylate radical, and

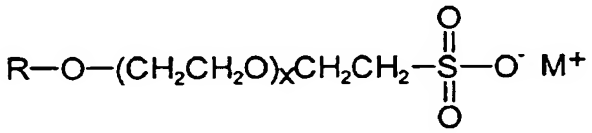
M^+ is sodium, potassium or ammonium counterion.

6. A detergent composition according to claim 5 wherein:

R_1 and R_2 are hydrogen, and R_3 is a carboxylate radical.

7. A detergent composition according to claim 2 wherein the major anionic surfactant constituent (A) consists solely of an alkyl ether sulfonate.

8. A detergent composition according to claim 7 wherein the anionic surfactant has the formula:



where:

R is a C_{4-22} linear or branched alkyl group,

x is an integer from 1 to 24, and

M^+ is alkali metal or ammonium counterion.

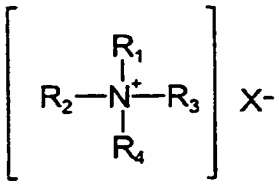
9. A detergent composition according to claim 8 wherein:

R is a C_{12-15} linear or branched alkyl group,

x is an integer from 1 to 10, and

M^+ is a sodium, potassium or ammonium counterion.

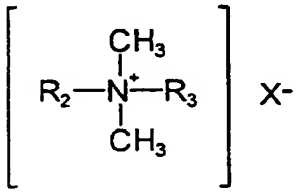
10. A detergent composition according to claim 2 wherein the quaternary ammonium surfactant (B) is one or more quaternary ammonium compounds and salts thereof according to the formula:



where at least one of R_1, R_2, R_3 and R_4 is a hydrophobic aliphatic, arylaliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the

entire cation portion of the molecule has a molecular weight of at least 165.

11. A detergent composition according to claim 10 wherein one or more quaternary ammonium compounds have the formula:



wherein:

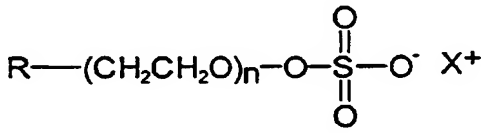
each R_2 and R_3 is selected from straight chained or branched C_8-C_{12}alkyl radicals;

or R_2 is selected from straight chained or branched $C_{12\text{-}16}$alkyl, $C_{8\text{-}18}$alkylethoxy, and

$C_{8\text{-}18}$alkylphenolethoxy radicals and R_3 is benzyl; and,

X is a halide or methosulfate.

12. A detergent composition according to claim 2 wherein the further anionic surfactant (F) is an alkyl ether sulfate or salt thereof according to the formula:



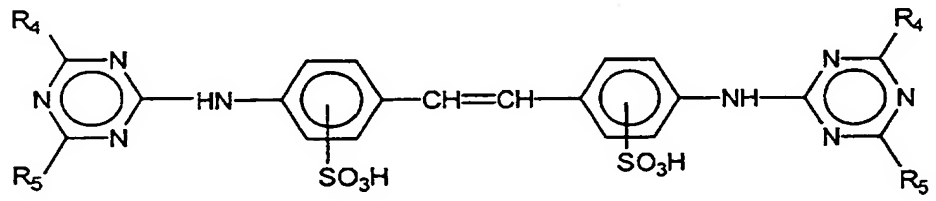
wherein R is a C_8 - C_{18} alkyl group;

n is an integer from 1 to 30; and

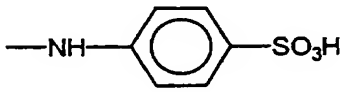
X represents an counterion selected from alkali metals and ammonium.

13. A detergent composition according to claim 2 wherein the compatible optical brightener (D) constituent is a stilbene based compound having three or more sulfate groups and/or sulfonic acid groups per molecule.

14. A detergent composition according to claim 13 wherein the optical brightener is a compound having the structure :



wherein R_4 and R_5 are selected from:



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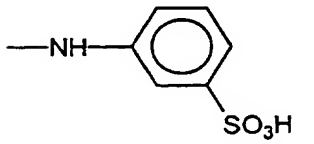

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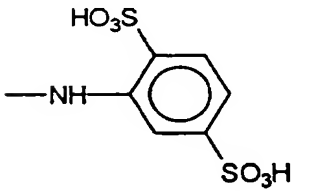

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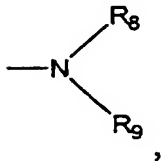

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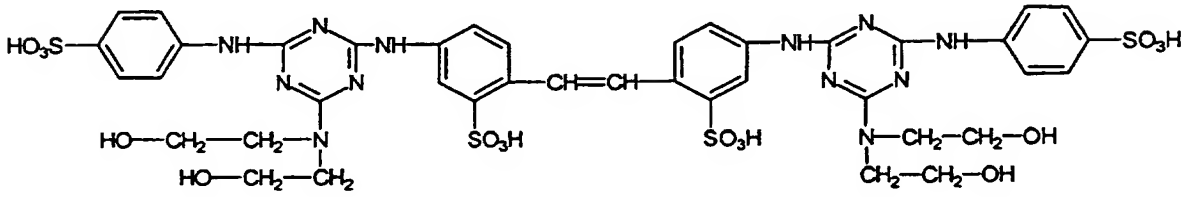
in which each of R_8 and R_9 is selected from hydrogen, lower alkyl, hydroxy and lower alkoxy.

15. A detergent composition according to claim 14 wherein the optical brightener has the structure:



16. A detergent composition according to claim 2 wherein the benzyl benzoate (E) is present in an amount of from 0.5% to 10% of the composition.

17. A process for laundering and sanitizing garments and textiles for killing dust mites infesting said garments or textiles, which process comprises the step of:

contacting the garments and textiles in an aqueous wash liquor containing an effective amount of a composition comprising:

A) 2 - 20 parts by weight of one or more anionic surfactants selected from alkyl ether carboxylates and alkyl ether sulfonate;

B) 1-25 parts by weight of one or more quaternary ammonium surfactant having germicidal properties;

C) 2-40 parts by weight of one or more nonionic surfactant selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, and alkanolamides;

D) 0.001-1 parts by weight of a compatible optical brightener constituent.

E) 0.3-15 parts by weight of benzyl benzoate; and

F) 0 -10 parts by weight of one or more further anionic surfactants selected from alkyl sulfates, alkyl sulfonates, alkyl ether sulfates, alkylaryl sulfonates, and alkylaryl ether sulfates which are present

in a proportion not to exceed one half of the weight of the one or more quaternary ammonium surfactants;

wherein the weight ratio of B:A is 1:2 or greater.

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Application No: GB 9919977.0
Claims searched: 1 to 17

Examiner: Michael Conlon
Date of search: 17 December 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C5D (D162, D182, D126)

Int Cl (Ed.6): C11D 3/00

Other: Online: EPODOC, WPI, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB2185992 A	(Colgate-Palmolive) Example 2 Table 6	1 - 17
X	EP0320848 A1	(Sterling Drug) claim 1 and the Examples	1 - 17
X	EP0133900 A2	(Sterling Drug) page 11, formulation E	1 - 17
X	US4576729	(Sterling Drug) Table 1	1 - 17

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.